Quantitative inhibiting effect of Group I-III cations on the growth of carbon nanotubes

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Quantitative inhibiting effect of Group I–III cations on the growth of carbon nanotubes**

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Main text

The concept of water-soluble supports for carbon nanotube (CNT) synthesis was first proposed by Liu et al. in 2002[1]. They showed that chemical vapor deposition (CVD) on a sodium chloride–supported cobalt catalyst using a methane carbon source at 600 ºC failed to grow carbon nanotubes, but produced carbon-encapsulated nanoparticles instead. It was concluded that the salt had a deactivating effect on the growth of nanotubes. Szabó et al. later showed, however, that limited amounts of multi-walled carbon nanotubes (MWCNTs) could be formed on a sodium chloride support using a cobalt catalyst and acetylene carbon source at 700 ºC [2]. Geng et al. have also shown that carbon nanofibers can be grown on sodium chloride using nickel and iron catalysts [3]. It is pertinent to consider why no single-walled carbon nanotubes (SWCNTs) were formed and why the carbon yields produced were so low. From an historical perspective, alkali metal salts are established promoters in CO_2 reforming of methane to produce synthesis gas (a mixture of CO and H_2). The process uses nickel catalysts that are deactivated by coking, and the metal salts are used to prevent this [4]. Carbon nanotubes, and particularly carbon fibers, can be components of coke. In this letter we report data showing that inorganic salts can inhibit carbon deposition to a quantitative degree, and we identify the mechanism most likely to cause the inhibition.

Sodium chloride melts at 800.8 ºC, so a CVD synthesis of CNTs requires some modification of the typical growth conditions [5]. A benchmark catalyst comprised of iron oxide nanoparticles supported on MgO (hereafter referred to as Fe-NP/MgO) was used, along with methane as the CVD carbon source. The iron oxide nanoparticles were prepared under argon, as follows. HCl (0.034 cm^3, 1.18 S.G.) was added to degassed water (2 cm^3) with stirring. To this was added $FeCl_3.6H_2O$ (0.35 g) and $FeCl_2.4H_2O$ (0.13 g). A second solution, consisting of ammonia (0.82 cm^3, 35 %) in degassed water (10 cm^3) was prepared and added to the first solution. The black suspension was stirred for 30 mins and the nanoparticles were then separated using a 13,000 Gauss magnet. The nanoparticles were washed successively with three 20 cm^3 portions of water, one 20 cm^3 portion of HCl (0.01 M) and two 20 cm^3 portions of ethanol. The iron content was determined by evaporation to be 7.9 mg cm^{-3}.

The powdered Fe-NP/MgO catalyst was doped with various quantities (0 to 0.5 wt %) of sodium chloride, and CVD was carried out at 750 ºC for 30 minutes using a mixture of methane (flow rate = 0.8 l min^{-1}) and hydrogen (flow rate = 0.2 l min^{-1}). The post-CVD products were found to have strikingly different visual appearances, with the carbon deposit ranging from black (at low NaCl content), through grey, to a barely perceptible shading (at the highest NaCl content). Thermogravimetric analysis (TGA) revealed a decreasing trend in carbon yield: see Fig. 1. Analysis by Raman spectroscopy (LabRam 300, 633 nm HeNe laser) indicated the D/G-band ratio was independent of the percentage of added sodium chloride, from which we infer that the NaCl inhibits *all* carbon formation, and does not selectively prevent either amorphous carbon deposition or

graphitic carbon nanotube growth. To our knowledge this is the first demonstration of a compound exhibiting a *quantitative* inhibiting effect on the growth of carbon nanotubes.

To investigate the spatial extent of inhibition, a quantity of the Fe-NP/MgO catalyst powder was compressed on to a silicon wafer. A crystal (~100 μm cube) of sodium chloride was then placed on top of the compressed support and CVD was again carried out at 750 ºC. Carbon deposit was observed on the catalyst, except for a ring around the sodium chloride crystal where the initial pale orange color of the catalyst could still be observed: see Fig. 2. The sodium chloride clearly inhibits carbon deposition within some range. Radial breathing modes (RBM) in Raman spectra of the carbon deposit, Fig. 3(a), indicate the presence of SWCNTs. By contrast, Raman spectra of the inhibited ring show no RBM, D-bands or G-bands; the only observable peaks arise from the catalyst and support. Scanning electron microscopy (SEM) analysis confirmed the presence of carbon nanotubes in the carbon deposit where bundles of nanotubes a few microns in length were observed sparsely scattered across the surface [6]. Carbon nanotubes were not observed in the inhibited ring. X-ray photoelectron spectroscopy (XPS) was employed to analyze the surface of the inhibited area, as shown in Fig. 3(b). No sodium peaks were detected, although this is likely to be due to the low sensitivity factors for sodium. However, a peak (2.6 at. %) attributable to chlorine 2p electrons was observed at 197 eV. This peak was not observed in the XPS spectrum of an unreacted control sample of Fe-NP/MgO catalyst powder. We have clear evidence that diffusion of atoms from the sodium chloride crystal to the surrounding catalyst is taking place during CVD.

Liu et al. noted two possible reasons for the inhibiting effect of sodium chloride [1]. First, it has been suggested that chlorine atoms could initiate radical reactions with both surface and gas-phase carbon species to create radical reaction sites on the growing graphitic layers [7]. We consider this implausible since chlorine is in the form of the chloride ion bound with cationic sodium. While we believe that diffusion of sodium chloride occurs, it is unlikely that free chlorine radicals exist in the gas phase. Second, it has been suggested that the thermal properties of sodium chloride influence the morphology of the carbon products. The build-up of a thermal gradient inside a catalytic metal particle has been recognized as a major driving force in the production of carbon filaments [8]. A relatively high diffusion coefficient and high thermal conductivity of sodium chloride might interfere with the build-up of such temperature gradients inside metal particles. This would result in the isotropic precipitation of carbon species on the nanoparticle surfaces, forming carbon-encapsulated nanoparticles. The second hypothesis fails to explain why carbon is not deposited in the immediate vicinity of sodium chloride crystals since it only explains the *type* of carbon growth. *We conclude that neither of the above suggestions can account for our observations.*

Either sodium chloride is inhibiting the formation of carbon or it is forming some reactive species that removes it. Since the reactor environment does not contain oxygen (which may have opened the

possibility for the formation of oxychloride species at elevated temperatures), we find the second possibility unlikely. At the elevated temperatures necessary for CVD, vaporization of sodium chloride from a crystal will occur. We suggest that sodium chloride diffuses from the sodium chloride crystal to the surrounding catalyst/support material and adsorbs at reactive step sites on metal nanoparticles [9]. The blockage of these sites suppresses carbon formation since they are required for the catalytic decomposition of methane to carbon. This explanation is consistent with our findings that smoother surfaces of compressed catalyst/support powder result in inhibited rings with greater diameters than rougher surfaces [6]; for a rougher surface the number of available nanoparticles will be greater.

To study the relative inhibiting effects of various metal salts, solutions of the metal salts LiCl, NaCl, KCl, $MgCl_2.6H_2O$, $CaCl_2$, $AlCl_3.6H_2O$ and Na_2SO_4) were prepared (5 cm^3, 0.143 mmol). For each metal salt, an aliquot (1 cm^3) of the solution was added to an aliquot of the iron oxide nanoparticle suspension (1 cm^3, to provide a metal loading of ~3 wt %) and MgO (0.263 g) in water (3 cm^3). The solvent was removed by evaporation and the samples were dried for 12 hours in an oven at 80 ºC before being reground. CVD was carried out at 900 ºC for 30 minutes using a mixture of methane (flow rate = 1.07 l min^{-1}) and hydrogen (flow rate = 0.76 l min^{-1}). Fig. 4 shows the results of TGA on the catalysts after CVD. All catalysts that contained additives showed a reduction in carbon deposit. We note that $CaCl_2$ appears to be most effective in inhibiting the CVD. Sodium chloride and sodium sulfate both show an inhibiting effect, indicating that suppression of carbon formation it is not solely an attribute of metal halides. The sulfate ion was used as a control because it was deemed unlikely to hinder carbon formation: sulfur has been used as a promoter of SWNT growth, and may aid growth by removing terminating species [10]. No substantial increase in the inhibiting effect was observed for the dichlorides or trichloride, confirming that carbon formation is not suppressed by simply increasing the number of moles of chloride ions: as would be expected if the chlorine-promoted nanoparticle deactivation theory of Liu et al. was correct.

The bulk-diffusion growth mechanism of carbon fibres proposed by Baker et al. [8], and applied to nanotube formation by Sinnott et al.[11], envisages dissolution of carbon into the metal nanoparticle followed by precipitation to form the graphitic nanotube. Precipitation occurs when the solubility limit of carbon in the metal is reached. This model is supported by Deck et al., who have observed that the carbon–metal binary phase diagrams of the nanotube-catalysing elements iron, cobalt and nickel show considerable similarities[12]. At 900 °C our Fe nanoparticles may indeed exist in the liquid state, and there may be sufficient energy to dissolve inorganic salts—such as sodium chloride—in these highly mobile metal nanoparticles. Decreasing the size of metal particles results in an increase in the ratio of surface to internal atoms, giving different physical and chemical properties as compared to the bulk material, e.g., lower melting temperatures and higher carbon solubilities. The effect of particle size on critical melting temperature, T_c, can be described by the equation

$$T_c = T_0 - \frac{2T_0}{\Delta H_{fusion}\rho_s r}\left[\sigma_{sl} + \left(1 - \frac{\rho_s}{\rho_l}\right)\sigma_l\right], \qquad (1)$$

where r is the particle radius, T_0 is the bulk melting temperature, ΔH_{fusion} is the latent heat of fusion, ρ_s is the density of the solid, ρ_l is the density of the liquid, σ_{sl} is the solid–liquid interfacial energy and σ_l is the surface energy of the liquid [13]. Eq. 1 is plotted in Fig. 5 for Fe nanoparticles. The critical diameters for an Fe nanoparticle are 9 nm at 750 °C and 11 nm at 900 ºC. Particles with diameters smaller than the critical diameter should exhibit liquid behaviour. The nanoparticles in our system that grow carbon nanotubes—in particular those at a suitable size for growing SWCNTs—should be considered as being in the liquid phase at both 750 and 900 °C.

Evidence to support the hypothesis that dissolved sodium ions inhibit growth can be found in the literature. Nizhenko et al. state that aluminium contents of up to ~40 wt % decrease the solubility of carbon in iron at 1550 °C almost to zero. They describe varying abilities to decrease carbon solubility in iron in the order Cu < Ga < Ge < Sn [14]. Gruzing and Protsenko et al. have also noted the effect of Al and Ni on reducing the solubility of carbon in iron [15, 16].

While we have shown there is some evidence to suggest that a decrease in the solubility of carbon in iron by addition of metal ions is plausible, it seems more likely that the inhibition effect we have observed is caused by blockage of reactive catalytic sites on the nanoparticle surface. The blocking mechanism would explain the inhibition of *all* types of carbon deposition (including nanotube formation) for solid or liquid metal nanoparticles. The inhibition of the surface catalytic decomposition of carbon species also explains why the effect is more observable with carbon sources that are more selective to catalytic decomposition: e.g., methane [1] compared with acetylene [2].

In conclusion, we have investigated the inhibition of carbon nanotube formation by simple inorganic salts, in particular sodium chloride. We find that the salt can inhibit growth quantitatively, which in its own right may be potentially useful for controlling CVD of carbon nanotubes. Our results suggest that carbon deposition is inhibited by the absorption of cations at reactive step sites on the nanoparticle surface, effectively blocking decomposition of the carbon source.

Figures

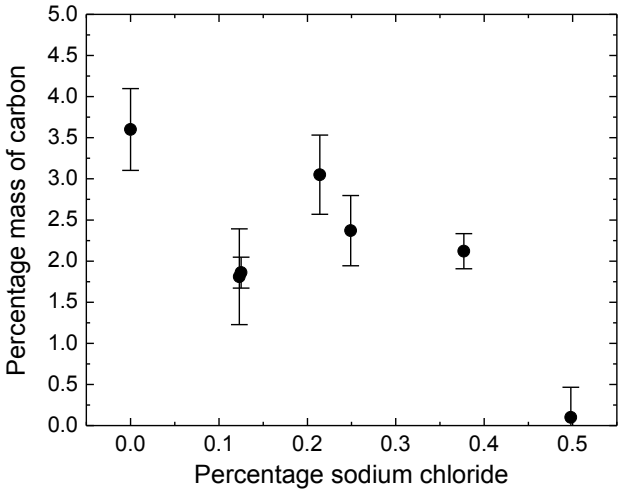

Fig. 1. Plot of percentage mass (wt %) carbon in samples grown by CVD (methane carbon source, 750 ºC) over Fe-NP/MgO catalysts doped with small amounts (wt %) of sodium chloride. The amount of carbon deposited decreases with increasing added sodium chloride.

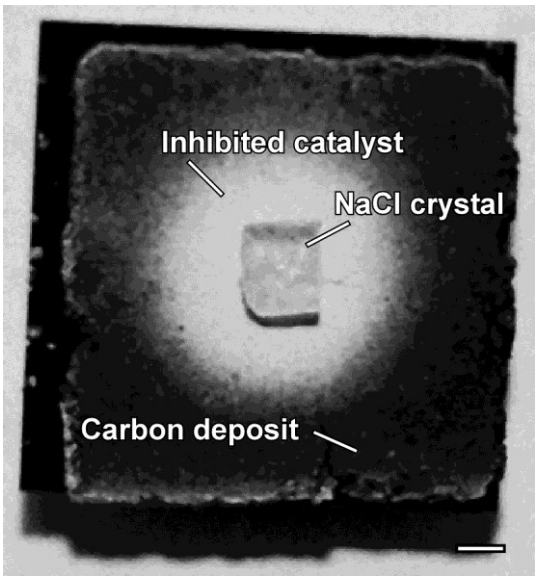

Fig. 2. Compressed Fe–NP/MgO catalyst powder with sodium chloride crystal after CVD (methane carbon source, 750 ºC). The black carbon deposit is inhibited around the sodium chloride crystal. Scale bar = 0.1 mm.

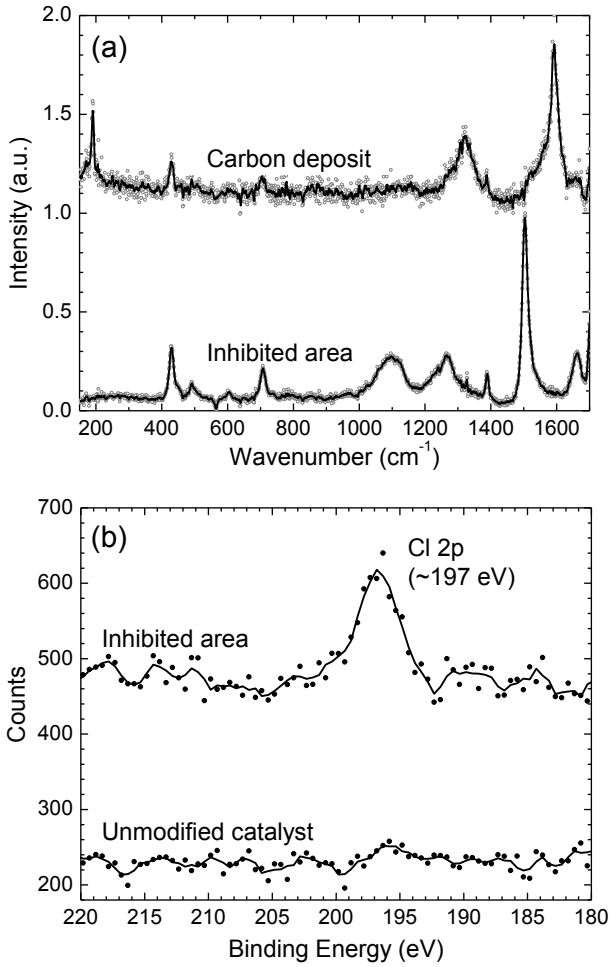

Fig. 3. (a) Raman spectra of carbon deposit and inhibited area as shown in Fig. 2. The indicators of single-walled nanotubes (intense G-band ~1600 cm^{-1}, low D-band ~1300 cm^{-1}, and RBMs ~190 cm^{-1}) are clearly present in the carbon deposit and absent in the inhibited area. The peaks in the spectrum of the inhibited area arise from the Fe-NP/MgO catalyst. (b) XPS spectra of inhibited area of catalyst containing NaCl crystal and a control, unmodified catalyst. A peak attributable to chlorine is only seen on the inhibited area (See Fig. 2).

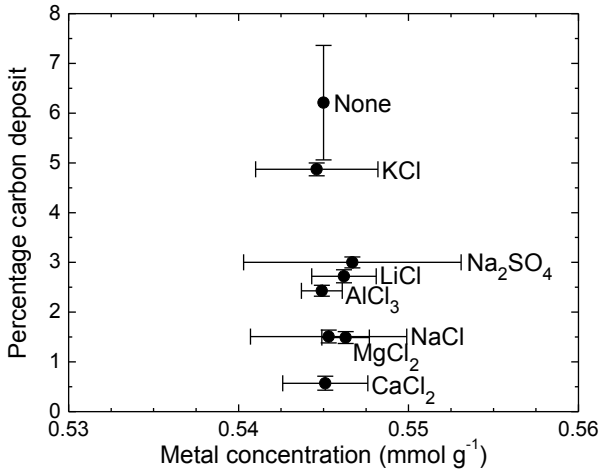

Fig. 4. Plot of carbon deposit against number of moles of metal in additive per gram of catalyst mixture. The horizontal error bars indicate the experimental uncertainties in the concentration of metal added to the catalyst/support mixture, as determined from weighing out metal salts (the inhibition effect is dependant on the concentration of inhibitor). The vertical error bars indicate the experimental uncertainties in the percentage carbon deposited as determined from TGA analysis.

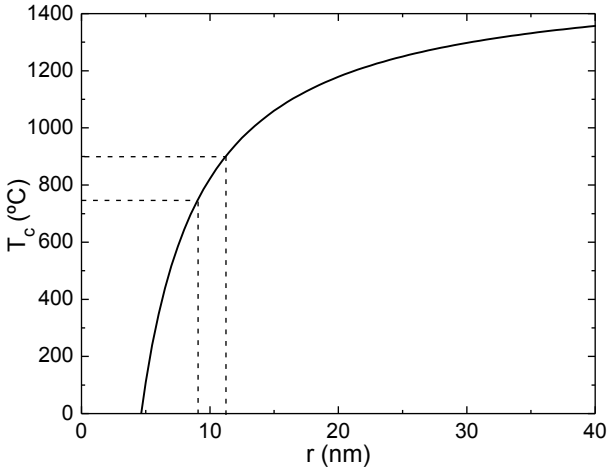

Fig. 5. Variation in the melting temperature of iron as a function of nanoparticle diameter, as described by Eq. 1 [13]. Dashed lines show particles at 750 ºC and 900 ºC.

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